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EP 0089202 A1

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(58) Field of search

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(54) Novel synergistic agricultural insecticidal and acaricidal combinations containing avermectin derivatives

(57) Novel combinations of agricultural insecticides, acaricides and pesticides have a synergistic effect against such agricultural insect and mite pests. Avermectin amino and alkylated amino derivatives thereof, which are known to be highly effective, broad-spectrum agricultural pesticidal agents, are combined with compounds which are known to be active as agricultural insecticidal and acaricidal agents such as organotin, pyrethroid, organocarbamate, organophosphorous, insect growth regulator, formamidine and chlorinated hydrocarbon compounds. Such avermectin derivatives may also be combined with chitin synthesis inhibitors, ovicides, metabolic inhibitors, feeding stimulants and natural insecticidal agents. In combination, effects are observed which are greater than what could be expected from the individual compounds. Compositions containing such a synergistic combination of compounds as active ingredients are also disclosed.

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TITLE OF THE INVENTION

NOVEL SYNERGISTIC AGRICULTURAL INSECTICIDAL AND
ARCARICIDAL COMBINATIONS

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BACKGROUND OF THE INVENTION

Avermectin compounds are a series of natural products isolated from the fermentation broth of a strain of Streptomyces avermitilis. The series consists of eight compounds, four major and four minor. The compounds are disclosed in U.S. Patent 4,310,519. Certain derivatives of such compounds are also disclosed, such as the 22,23-dihydro derivatives described in U.S. Patent 4,199,569. The 13-deoxy derivatives of avermectin compounds are disclosed in U.S. Patents 4,171,314 and 4,173,571. The 4"-phosphate derivatives of the avermectin compounds with a 13-O-disaccharide group present, are disclosed in US Patent 4,469,682. In addition, the 4"-amino compounds and the 4"-alkylated amino compounds, the avermectin compounds of the instant combination, are disclosed in US patent 4,427,663.

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The synergistic combinations also include organotin compounds such as Plictran (cyhexatin) and Vendex (fenbutatin oxide) disclosed in The 1981 Farm Chemicals Handbook, pages 268 and 359, respectively; synthetic pyrethroids, such as Ambush or Pounce (permethrin), Ammo or Cymbush (cypermethrin) and Pydrin or Belmark (fenvalerate), disclosed in The 1981 Farm Chemicals Handbook, pages C256, C95 and C148, respectively; chitin synthesis inhibitors such as Dimilin (diflubenzuron) disclosed in US patents; 3,748,356, 3,933,908, 3,989,842, and The 1981 Farm Chemicals Handbook, page C115, and Nomolt (teflubenzuron) disclosed in Technical Information Sheet of CME134 Celamerck, Ingelheim/Rhein, Germany; ovicides such as Savey (hexythiazox) disclosed in The 1987 Farm Chemicals Handbook, page C137, and Apollo (clofentezine) disclosed in The 1987 Farm Chemicals Handbook, page C64; metabolic inhibitors such as Butacide (piperonyl butoxide) disclosed in The 1987 Farm Chemicals Handbook, pages E20 and E78, triphenyl phosphate disclosed in US patent 2,805,240; feeding stimulants such as Coax disclosed in The 1987 Farm Chemicals Handbook, page C65; and natural insecticides such as Dipel (Bacillus thuringiensis) as disclosed in J. Agr. Food Chem 7, 687 (1959); organocarbamate compounds, such as Lannate (methomyl) disclosed in The 1981 Farm Chemicals Handbook, page C215, Larvin (thiodicarb) disclosed in The 1987 Farm Chemicals Handbook, pages C250 and E72, and Furadan (carbofuran) disclosed in The Pesticide Manual, Worthing (Ed.) (1979) page 82; organophosphorous compounds, such as Orthene (acephate), Lorsban

(chlorpyrifos), Thimet (phorate), Basudin (diazinon) and methylparathion disclosed in The 1981 Farm Chemicals Handbook, pages C246, C77, C262, C107 and C218, respectively; malathion, disclosed in The 1987 Farm Chemicals Handbook, pages C155 and E66, dimethoate disclosed in The 1987 Farm Chemicals Handbook, pages C91 and E23, and Padan (cartap) disclosed in The Pesticide Manual, Worthing (Ed.) (1979) page 86; insect growth regulators, such as Dimilin (diflubenzuron), also useful as an chitin synthesis inhibitor and discussed above; formamidine compounds, such as Mitac (amitraz) and Fundal (chlordimeform) disclosed in The 1981 Farm Chemicals Handbook, pages C17 and C70, respectively, and chlorinated hydrocarbon compounds such as Kelthane (dicofol) and Acarol (bromopropylate) disclosed in The 1981 Farm Chemicals Handbook pages C110 and C115, respectively, and Thiodan (endosulfan) disclosed in US patent 2,983,732.

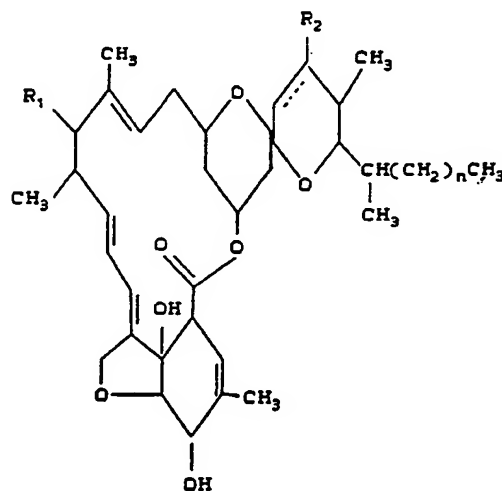
SUMMARY OF THE INVENTION

The instant disclosure describes certain synergistic combinations of avermectin compounds and organotin, pyrethroid, chitin synthesis inhibitor, ovicide, metabolic inhibitor, feeding stimulant, organocarbamate, organo-phosphorous, insect growth regulator, formamidine, tertiary amine and chlorinated hydrocarbon compounds and natural insecticidal agents which are referred to hereinafter as "combining compounds". Thus, it is an object of this invention to describe such synergistic combinations. It is a further object to describe the individual components of such synergistic

combinations and the relative proportion of each component in the combination. A still further object of this invention is to describe the agricultural, insecticidal, acaricidal and pesticidal effects of such combinations. Further objects will become
5 apparent from a reading of the following description.

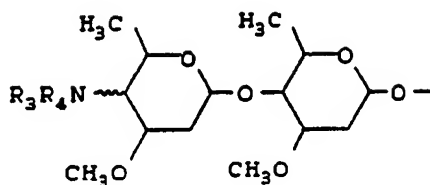
DESCRIPTION OF THE INVENTION

The instant invention consists of a combination of avermectin compounds and combining
10 compounds which have a synergistic effect when used in the control or elimination of infestations in domestic and agricultural environments. The avermectin compounds of this invention have the
15 following formula:



wherein n is 0 or 1;

R₁ is



10 R₂ is hydrogen;

the broken line indicates a single or a double bond;
however, R₂ is present only when the broken line
indicates a single bond; and

R₃ and R₄ are independently hydrogen or loweralkyl.

15 The preferred avermectin compound is the
4"-epimethyl amino derivative of avermectin Bla/Blb.
That is the compound wherein R₃ is hydrogen, R₄ is
methyl; the 4"-amino stereochemistry is β, above the
plane of the ring (the natural stereochemistry for the
20 avermectin is α, below the plane of the ring); and n
is both 0 and 1, that is the compound which is a
mixture of the sec. butyl compound (n = 1) and the
isopropyl compound (n = 0), in approximately an 80:20
ratio of sec-butyl to isopropyl compounds.

25 The combining compounds that constitute the
second part of the instant synergistic combinations
are exemplified by the representative compounds
disclosed above in the Background of the Invention.

30 When used as agricultural insecticide or
miticides the avermectin compounds are administered
at dosage rates of from 1.0 to 50 g of the active

compound per hectare. When used as agricultural insecticide agents the combining compounds are administered at dosage rates of from 10 to 2500 g of the active compound per hectare.

5 The synergistic effects of the combination of the avermectin compounds with the combining compounds are observed in providing for a reduced dosage of one or both of the components. Thus, a
10 lessened quantity of the agricultural insecticide or acaricide is administered than normally would be required which results in a lessening of possible side effects and a lessening in the development of resistance. In addition, there is observed the synergistic expansion of the spectrum of activity on
15 agricultural insect or mite pests which may be successfully combatted than would be expected from a consideration of the spectra of activity of the individual components. Thus, the possibility of eliminating agricultural insect and mite infestations
20 against which the individual components are ineffective or only partially effective is realized in the instant synergistic combination.

 The agricultural arthropod infestations against which the instant synergistic combination is
25 particularly effective are Acarina such as Tetranychus urticae, Panonychus ulmi, Panonychus citri, Phyllocoptruta oleivora and Polyphagotarsonemus latus; and the like; Coleoptera such as Leptinotarsa decemlineata, Phyllotreta striolata; Lepidoptera such
30 as Spodoptera exigua, Plutella xylostella, Pieris rapae, Heliothis virescens and H. zea; Diptera such as Liriomyza trifolii; Homoptera such as Psylla pyricola, Myzus persicae, Brericoryne brassicae,

Bemisia tabaci and Aphis gossypii, and the like;
Orthoptera such as Blattella germanica.

5 The instant synergistic combination is
useful for controlling the above mite pests, and
others, on economically useful crops such as maize,
vegetables, cotton, deciduous fruit, citrus, tree
nuts and vines.

10 In using the instant synergistic combination,
the individual components are used in proportions
which may extend to from 1 part of the avermectin
compound to 2500 parts of combining compound to from
100 parts of the avermectin compound to 1 part of
combining compound.

15 The synergistic composition is useful
against insect and mite pests of stored grain and
agricultural plants and immature stages of mites or
insects living in or on plant tissue. When the
synergistic composition is used to combat
agricultural pests that inflict damage upon crops
while they are growing or in storage, it is applied
20 using known techniques such as sprays, granules,
dusts, emulsions, and the like, to the growing plant
or the soil in which it is planted, or to the stored
crops to effect protection from such agricultural
pests.

25 Specific formulations containing avermectin
compounds and combining compounds which have
synergistic agricultural, insecticidal, acaricidal,
pesticidal and miticidal effects are as follows:

	<u>Formulation 1</u>	<u>Weight %</u>
	4"-epimethylamino-4"-deoxy	2.00
	Avermectin Bla/Blb	
	Dicofol	20.00
5	Xylenes	60.00
	Emulsifier	<u>18.00</u>
	Total	100.00
	<u>Formulation 2</u>	<u>Weight %</u>
10	4"-epimethylamino-4"-deoxy	2.00
	Avermectin Bla/Blb	
	Acarol	24.00
	Xylenes	56.00
	Emulsifier	<u>18.00</u>
15	Total	100.00
	<u>Formulation 3</u>	<u>Weight %</u>
	4"-epimethylamino-4"-deoxy	2.00
	Avermectin Bla/Blb	
20	Chlorbenzilate	15.50
	Xylenes	65.50
	Emulsifier	<u>17.00</u>
	Total	100.00
25	<u>Formulation 4</u>	<u>Weight %</u>
	Chlordimeform	24.0
	4"-epimethylamino-4"-deoxy	2.2
	Avermectin Bla/Blb (91%)	
	Xylenes	61.8
30	Emulsifiers	<u>12.0</u>
	Total	100.0

	<u>Formulation 5</u>	<u>Weight %</u>
	Amitraz	20.0
	4"-epimethylamino-4"-deoxy	2.2
	Avermectin Bla/Blb (91%)	
5	Xylenes	65.8
	Emulsifiers	<u>12.0</u>
	Total	100.0
	<u>Formulation 6</u>	<u>Weight %</u>
10	Malathion	20.0
	4"-epimethylamino-4"-deoxy	2.2
	Avermectin Bla/Blb (91%)	
	Xylenes	65.8
	Emulsifiers	<u>12.0</u>
15	Total	100.0
	<u>Formulation 7</u>	<u>Weight %</u>
	Dimethoate	20.0
	4"-epimethylamino-4"-deoxy	2.2
20	Avermectin Bla/Blb (91%)	
	Xylenes	65.8
	Emulsifiers	<u>12.0</u>
	Total	100.0
	<u>Formulation 8</u>	<u>Weight %</u>
25	Dimilin (98%)	25.5
	4"-epimethylamino-4"-deoxy	2.0
	Avermectin Bla/Blb (91%)	
	Attaclay	25.0
30	Diethylene glycol	4.0
	Talc	28.0
	Wetting agent	12.0
	Dispersing agent	3.0
	Oleic acid	<u>0.5</u>
	Total	100.0

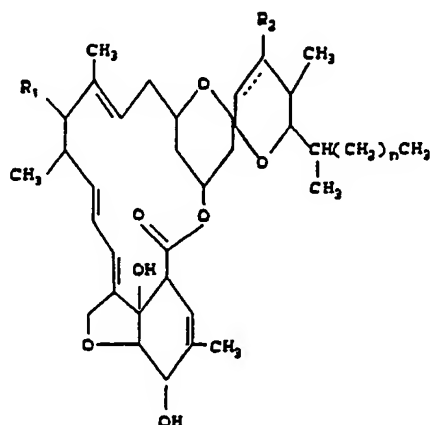
	<u>Formulation 9</u>	<u>Weight %</u>
	Dimilin (98%)	4.08
	4"-epimethylamino-4"-deoxy	0.44
	Avermectin Bla/Blb (91%)	
5	Granular Montmorillonite Clay	89.48
	Diethylene glycol	<u>6.00</u>
	Total	100.00
	<u>Formulation 10</u>	<u>Weight %</u>
10	Diazinon (87%)	54.0
	4"-epimethylamino-4"-deoxy	2.2
	Avermectin Bla/Blb (91%)	
	Xylenes	29.8
	Emulsifier	<u>14.0</u>
15	Total	100.0
	<u>Formulation 11</u>	<u>Weight %</u>
	Methyl Parathion (80%)	25.0
	4"-epimethylamino-4"-deoxy	2.2
20	Avermectin Bla/Blb (91%)	
	Xylenes	60.8
	Emulsifier	<u>12.0</u>
	Total	100.0
	<u>Formulation 12</u>	<u>Weight %</u>
25	Chlorpyrifos	24.0
	4"-epimethylamino-4"-deoxy	2.2
	Avermectin Bla/Blb (91%)	
	Xylenes	61.8
30	Emulsifier	<u>12.0</u>
	Total	100.0

	<u>Formulation 13</u>	<u>Weight %</u>
	Diazinon (87%)	5.75
	4"-epimethylamino-4"-deoxy	0.33
	Avermectin Bla/Blb (91%)	
5	Montmorillonite granule	87.92
	Diethylene glycol	<u>6.00</u>
	Total	100.00
	<u>Formulation 14</u>	<u>Weight %</u>
10	Methomyl	24.0
	4"-epimethylamino-4"-deoxy	2.2
	Avermectin Bla/Blb (91%)	
	Attaclay	36.3
	Kaolin	16.0
15	Wetting agent	12.0
	Dispersing agent	3.0
	Oleic acid	0.5
	Diethylene glycol	<u>6.0</u>
	Total	100.0
20	<u>Formulation 15</u>	<u>Weight %</u>
	Carbofuran	50.0
	4"-epimethylamino-4"-deoxy	2.2
	Avermectin Bla/Blb (91%)	
25	Attaclay	19.8
	Kaolin	6.5
	Wetting agent	12.0
	Dispersing agent	3.0
	Oleic acid	0.5
30	Diethylene glycol	<u>6.0</u>
	Total	100.0

	<u>Formulation 16</u>	<u>Weight %</u>	<u>Weight %</u>	
	4"-epimethylamino-4"-deoxy	2.2	2.2	
	Avermectin Bla/Blb			
	Plictran	50.0	-	
5	Vendex	-	50.0	
	Attaclay	25.0	25.0	
	Kaolin	3.8	3.8	
	Diethylene glycol	4.0	4.0	
	Wetting agent	12.0	12.0	
10	Dispersing agent	<u>3.0</u>	<u>3.0</u>	
	Total	100.0	100.0	
	<u>Formulation 17-Liquid</u>	<u>Weight %</u>	<u>Weight %</u>	<u>Weight %</u>
	4"-epimethylamino-4"-	2.2	2.2	2.2
15	deoxy Avermectin			
	Bla/Blb (91%)			
	Cypermethrin	20.0	-	-
	Fenvalerate	-	20.0	-
	Deltamethrin	-	-	20.0
20	Xylenes	70.0	70.0	70.0
	Emulsifier	<u>8.0</u>	<u>8.0</u>	<u>8.0</u>
	Total	100.0	100.0	100.0
	<u>Formulation 18-Granular</u>	<u>Weight %</u>	<u>Weight %</u>	<u>Weight %</u>
25	4"-epimethylamino-4"-	0.33	0.33	0.33
	deoxy Avermectin			
	Bla/Blb (91%)			
	Avermectin Bla/Blb (91%)	0.33	0.33	0.33
	Cypermethrin	3.00	-	-
30	Fenvalerate	-	3.00	-
	Deltamethrin	-	-	3.00
	Montmorillonite granule	90.67	90.67	90.67
	Diethylene glycol	<u>6.00</u>	<u>6.00</u>	<u>6.00</u>
	Total	100.00	100.00	100.00

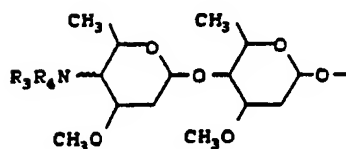
WHAT IS CLAIMED IS:

1. A synergistic agricultural,
insecticidal, acaricidal and pesticidal combination
of an avermectin compound having the formula:



wherein n is 0 or 1;

R₁ is



R₂ is hydrogen;

the broken line indicates a single or a double bond;

however, R₂ is present only when the broken line

indicates a single bond; and R_3 and R_4 are independently hydrogen or lower alkyl; and a combining compound selected from the group consisting of organotin, pyrethroid, chitin synthesis inhibitor, ovicide, metabolic inhibitor, feeding stimulant, organocarbamate, organophosphorous, insect growth regulator, formamidine, chlorinated hydrocarbon, and natural insecticidal agents.

2. The synergistic combination of Claim 1 wherein the organotin compound is cyhexatin or fenbutatin oxide; the pyrethroid compound is permethrin, cypermethrin, fenvalerate or deltamethrin; the chitin synthesis inhibitor is diflubenzuron or teflubenzuron; the ovicide is hexythiazox or clofentezine; the metabolic inhibitor is piperonyl butoxide or triphenyl phosphate; the feeding stimulant is coax; the natural insecticide is *Bacillus thuringiensis*; the organocarbamate compound is methomyl, dithiocarb or carbofuran; the organophosphorous compound is acephate, chlorpyrifos, phorate, diazinon, methylparathion, malathion, dimethoate; the tertiary amino is cartap; the insect growth regulator compound is diflubenzuron; the formamidine compound is amitraz or chlordimeform, and the chlorinated compound is dicofol, bromopropylate, or endosulfan wherein the compounds are present at a proportion of from 1 part of the avermectin compound to 2,500 parts of combining compound, to from 100 parts avermectin compound to 1 part of combining compound.

3. A method for the treatment of
agricultural insect and mite infestations which
comprises applying to an agricultural crop or
commodity infected with insects or mites, the
synergistic combination of Claim 1.

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